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Published in:
Synthetic Metals

DOI:
10.1016/S0379-6779(02)01123-2

ELSEVIER

Synthetic Metals 137 (2003) 881–882

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Processible conducting nanoscale cylinders due to self-organized polyaniline supramolecules

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Abstract

Polyaniline sulphonates contain hydrogen bonding acceptor sites, which allow construction of supramolecules and self-organized structures. Here we have characterized the phase behavior of complexes of polyaniline, camphorsulphonic acid (CSA) and 4-hexylresorcinol (Hres), PANI(CSA)$_x$(Hres)$_y$, using small-angle X-ray scattering (SAXS) and electrical conductivity. A hexagonal cylindrical structure with period around 35 Å allows plastication due to the flexible side chains. The conductivity of complexes increased when CSA or Hres were added to the nominal complex PANI(CSA)$_{0.5}$ indicating that CSA and Hres can be co-solvents for PANI(CSA)$_{0.5}$.

Keywords: polyaniline, self-organization, supramolecular

1. Introduction

Nature has ability to form self-organized functional materials based on competing interactions. Same kind of ideas has been realized also in synthetic polymers in order to form micro-scale functional materials [1-4]. Block copolymers form self-organized spherical, cylindrical, gyroid, and lamellar structures with length scale of 100 – 1000 Å [5] but also comb-shaped copolymers with repulsive side chains allow self-organization [6]. Covalent connections between backbone and repulsive side chains can be replaced with weaker physical bonds, such as ionic interactions [7,8], coordination [9] and hydrogen bonds [10,11] leading to plastization of rigid polymer backbones [12]. Typically the length scale of these supramolecular structures is 20 – 50 Å and both cylindrical and lamellar organization has been observed [10,11].

2. Results and Discussion

Polyaniline emeraldine base protonated with strong acid such as CSA forms highly conducting polymer salt, especially cast from hydrogen bonding m-cresol. Hres, in turn, has a longer alkyl chain with two hydrogen bonding hydroxyl groups enabling self-organized structures. Here we have investigated the effect of the number of CSA x and Hres y molecules *vs.* aniline repeat unit, i.e. x = 0.5, 0.75, and 1.0 and y = 0, 0.5, 1.0, 1.5, and 2.0, on self-organization and conductivity. The SAXS intensity patterns of the complexes are represented in Fig. 1. Some of the complexes have sharp peaks ($1q_1$, $\sqrt{3}q_1$ and $2q_1$) indicating a hexagonal cylindrical structure with a long period around 35 Å. It was observed that the period of complexes does not change considerably as a function of the mole fraction of Hres and CSA. In addition, when the amount of CSA increases, more Hres is needed, in order to obtain well-developed structures (Fig.1). Pure Hres has a sharp peak at 0.29 Å^{-1} and when the mole fraction of Hres y is 1.5 or 2.0, another flat intensity maximum appears at ca. 0.3 Å^{-1} indicating that the attraction between PANI(CSA)$_x$ and Hres is not anymore strong enough and the sample is partly phase separated. The intensity of this flat peak also increases with x. SAXS measurements were also made for PANI(CSA)$_{0.5}$(Hres)$_{1.0}$ as a function of temperature and order-disorder transition (ODT) was observed at ca. 130°C. Conductivity of PANI(CSA)$_{0.5}$(Hres)$_y$ complexes increased about two decades up to 1 S/cm when the mole fraction of Hres increased and cylindrical structure was formed.

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0379-6779/03/$ – see front matter
doi:10.1016/S0379-6779(02)01123-2

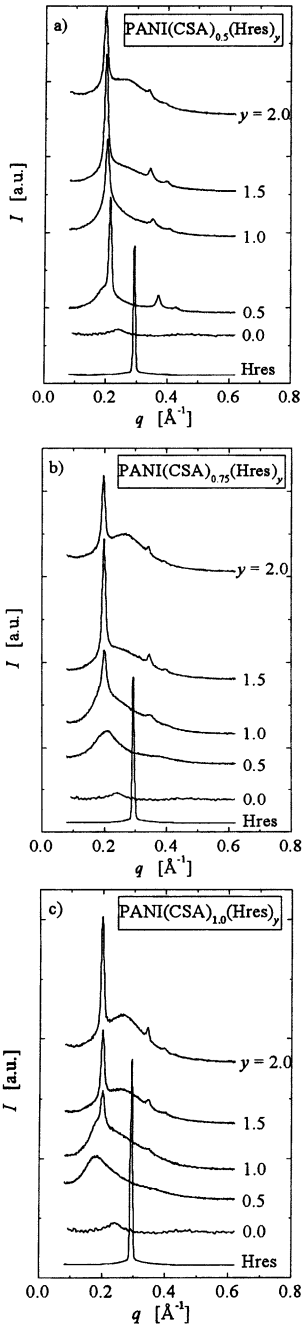

Fig 1. SAXS intensity patterns of $PANI(CSA)_x(Hres)_y$ complexes for a) $x = 0.5$, b) $x = 0.75$, and c) $x = 1.0$ after annealing at 105 °C indicates the formation of cylindrical structure.

On the other hand, same kind of effect was observed when the mole fraction of CSA increased (Fig. 2). This indicates that both CSA and Hres as strong hydrogen bonding donors, can be co-solvent for $PANI(CSA)_{0.5}$. Conductivity measurements were also made for complex $PANI(CSA)_{0.5}(Hres)_{1.0}$ as a function of temperature. Conductivity did not change at ODT (130 °C), which qualitatively confirms that increased conductivity of nominal complex $PANI(CSA)_{0.5}$ with x and y is due to the ability of Hres and CSA to act as co-solvent for $PANI(CSA)_{0.5}$.

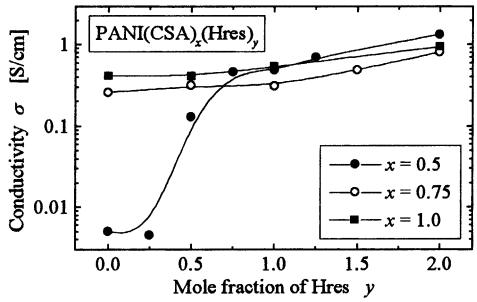

Fig 2. DC-conductivity of $PANI(CSA)_x(Hres)_y$ complexes as a function of the mole fraction of Hres.

3. Conclusions

Electrically conducting polyaniline salt forms ordered "nanowires" based on hydrogen bonding with Hres ($L_p \approx$ 35 Å). Conductivity of nominal complex, $PANI(CSA)_{0.5}$, increased with addition of CSA and Hres. Conductivity didn't at ODT, which also qualitatively confirms that both CSA and Hres can be co-solvents for $PANI(CSA)_{0.5}$.

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